

Final report for Department of the Army Contract # DAAL01-95-K-0061

Title:

Photofragmentation Studies of an Energetic Materials Sensor Based on a Laser  
Photofragmentation/Fragment Detection Approach

Purpose:

The goals of this research project were to:

1. perform spectroscopic studies of the key fragment species NO and NO<sub>2</sub> and identify suitable wavelength schemes for photofragmentation (PF) and fragment detection (FD) by a laser induced fluorescence (LIF) approach;
2. perform a survey of the pertinent literature to identify instrumental features that are desirable for PF/LIF sensors.

Results and Discussion:

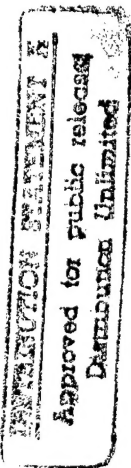
A primary objective of this project was to identify and characterize several wavelength schemes for their utility for measuring trace levels of nitrocompounds. The schemes were assessed using NO and NO<sub>2</sub> vapors as these species are the fragments that are produced and ultimately detected in the PF/LIF approach. NO and NO<sub>2</sub> are each detected by the laser induced fluorescence signals of NO via multiphoton excited fluorescence. In this technique, a focussed laser beam is used to excite NO by way of a two or three photon absorption, i.e. the energy between the initial and final states corresponds to the sum of two or three photons. Fluorescence emission from the excited is detected and used to quantify the amount of NO (or NO containing molecule) present.

Criteria for selecting possible excitation wavelengths include: strong or highly efficient multiphoton absorption at the excitation wavelength; the wavelength should be readily accessible to commercial laser instrumentation; the wavelength should be compatible with fiber optic transmission over long distances (tens of meters). The first criterion indicates that the laser wavelength should correspond to an allowed two or three photon absorption to a low lying excited state of NO. The second and third criteria suggest that the laser excitation wavelength should fall within the near UV to visible regions of the spectrum.

Several wavelength regions were investigated for their analytical utility for detecting nitrocompounds by the PF/LIF approach. The utility of each scheme was assessed using simple mixtures of NO and NO<sub>2</sub> in N<sub>2</sub> gas. The first wavelength region investigated was near 410 nm which corresponds to two photon excitation of A<sup>2</sup>Σ<sup>+</sup>-X<sup>2</sup>Π (2,0) transitions of the NO molecule.<sup>1,2,3</sup> Fluorescence emissions of NO were observed throughout the region 200-300 nm, the strongest of which corresponded to the A-X (0,0) and (0,1) bands at 226 nm and 237

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nm, respectively. For all future measurements, fluorescence emissions were monitored at 237 nm. Although NO and NO<sub>2</sub> could both be observed using excitation at 410 nm followed by fluorescence emission at 237 nm, the signal to noise of the measurements for these two species were not judged to be sufficiently high to be useful for the proposed application. Consequently other schemes were investigated.

The next wavelength scheme investigated corresponded to two photon excitation via the C<sup>2</sup>Π-X<sup>2</sup>Π transitions near 381 nm.<sup>3,4,5</sup> Although the laser energy at this wavelength is considerably less than that available at 410 nm, the two photon absorption probability is higher at 381 nm resulting in efficient two photon excitation. Although it was hypothesized that strong fluorescence emissions from the excited NO molecules would be observed in the far UV near 190 nm (corresponding to C-X (0,0) emissions) due to the short radiative lifetime of the C state, these emissions were not observed. Instead strong emissions from the A state at 237 nm were observed indicating that nonradiative decays rapidly transferred population from the C state to the A state. Efficient nonradiative decay from the C state to the A state has been observed previously and was found to be significant even at relatively low pressures (< 10 torr).<sup>3</sup> As all of the measurements in the current studies were performed at atmospheric pressure, the population transfer rate is expected to be high. High sensitivity measurements of NO and NO<sub>2</sub> were possible using C-X excitation at 381 nm and fluorescence detection at A-X 237 nm (Figures 1 and 2). The PF/LIF response was evaluated over a range of concentrations and the sensitivity and limit of detection was evaluated for NO and NO<sub>2</sub> and found to be 2 ppm for both species. It is expected that even higher sensitivity could be achieved for higher laser pulse energies and for a better fluorescence collection efficiency.

One aspect of using laser excitation at 381 nm was that equivalent sensitivities were obtained for NO and NO<sub>2</sub>. It would be preferable to use a PF/LIF approach that could selectively respond to NO<sub>2</sub> in order to differentiate the NO<sub>2</sub> signal from ambient sources of NO. One way to accomplish this would be to use a scheme that only detected vibrationally excited NO which would be present as a result of NO<sub>2</sub> photolysis but would be insensitive to ambient NO which would only be present in the ground vibrational state. This strategy was tested using laser excitation near 475 nm which was hypothesized to correspond to two photon excitation of NO via the A-X (0,1). Strong PF/LIF signals were observed for NO<sub>2</sub> using this approach (Figure 3). Unfortunately, strong signals were also observed for NO which indicated that the excitation was not likely to correspond to the hypothesized two photon scheme (Figure 4). It is believed that excitation near 475 nm corresponds to three photon excitation of NO via the F<sup>2</sup>Δ-X<sup>2</sup>Π (0,0), H<sup>2</sup>Δ-X<sup>2</sup>Π (0,0) and H'<sup>2</sup>Π-X<sup>2</sup>Π (0,0) bands.<sup>6</sup> Despite the fact that strong fluorescence emissions were observed for this excitation wavelength, the sensitivities were not significantly higher than those achieved at 381 nm. Furthermore it was difficult to achieve a linear response as a function of concentration, presumably due to the higher power dependence of the excitation process. Further investigations of this wavelength were not pursued.

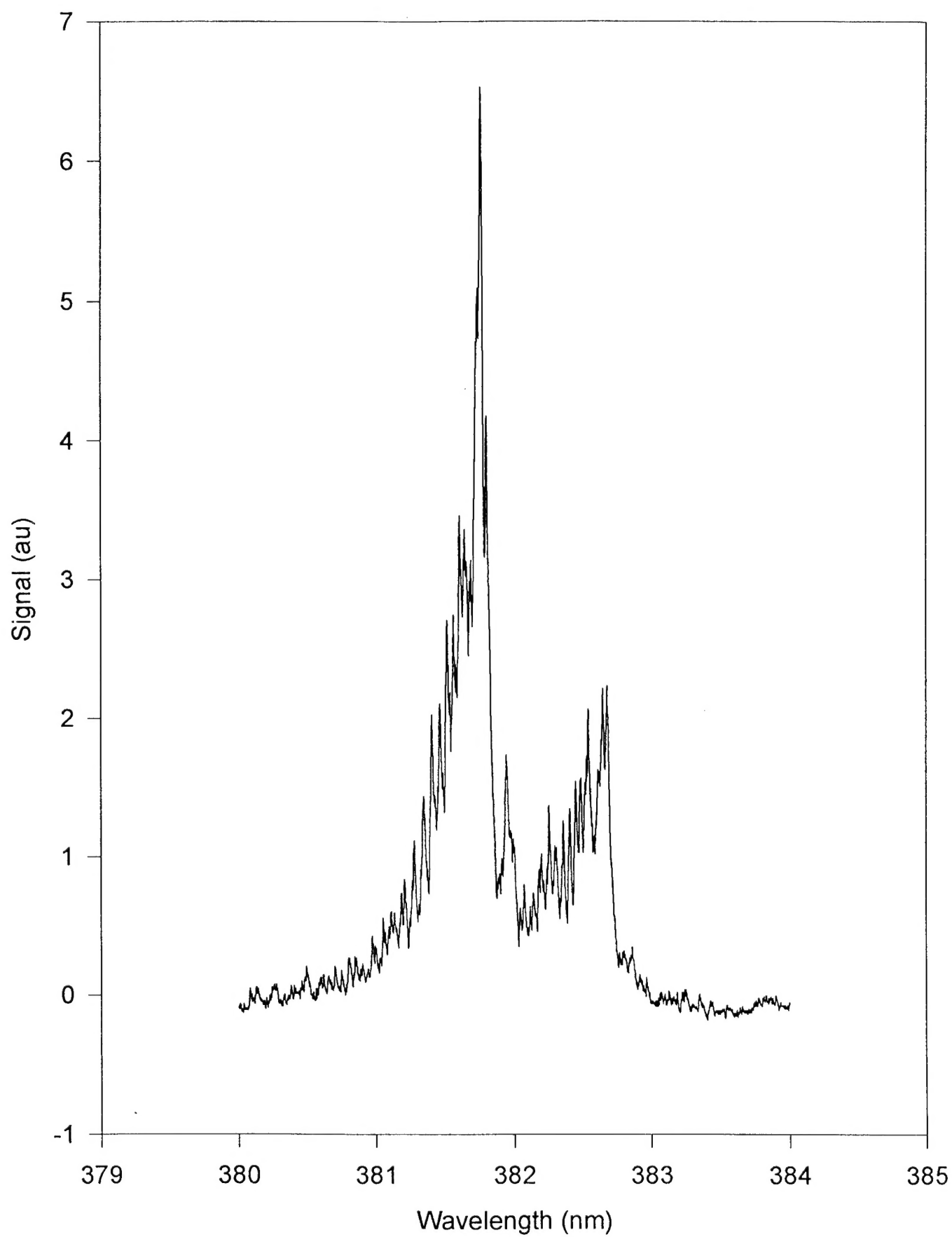
The other primary goal of this project was to perform a literature survey of photofragmentation techniques. The results of this survey have been documented in a literature review that was prepared in collaboration with Dr. R.C. Sausa of the US Army Research Laboratory, Aberdeen Proving Ground and was recently published in the open

literature (Applied Spectroscopy Reviews 31, 1-72, 1996). This literature review has resulted in the identification of several photofragmentation strategies which may prove useful for the real time detection of nitrocompounds (energetic materials) in the vapor phase. A copy of the title page and abstract of this review is included at the end of this report.

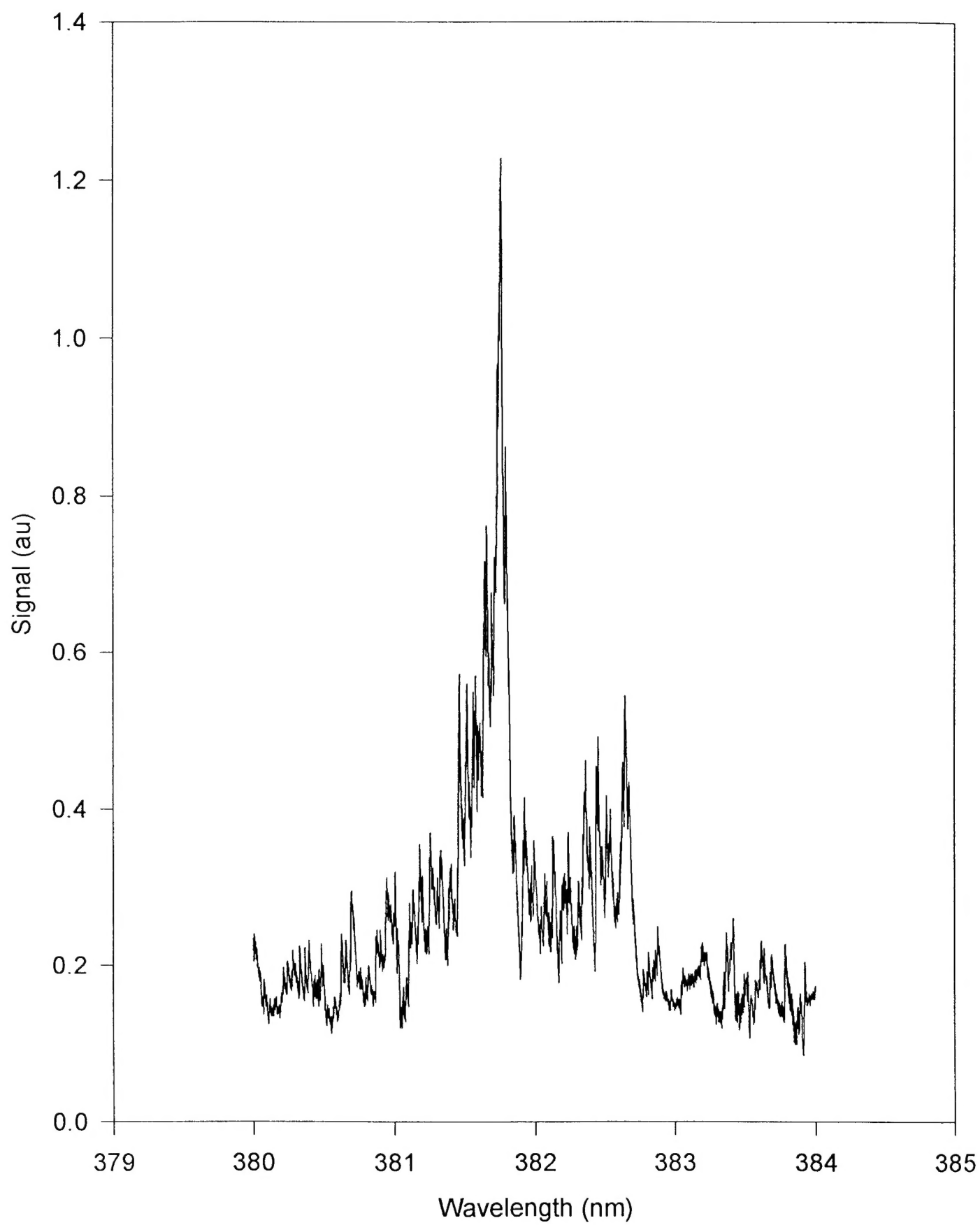
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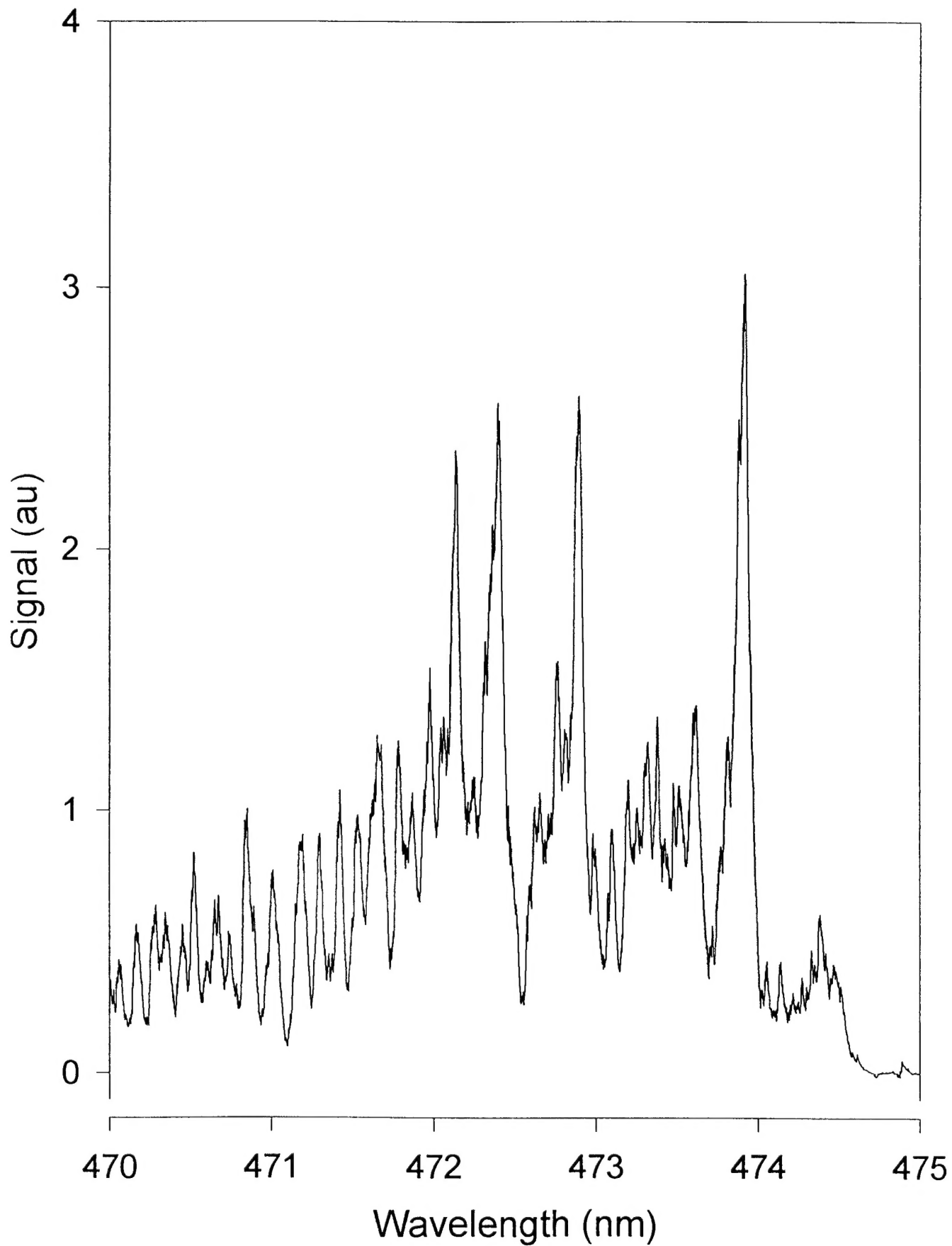
NO C-X(0,0)



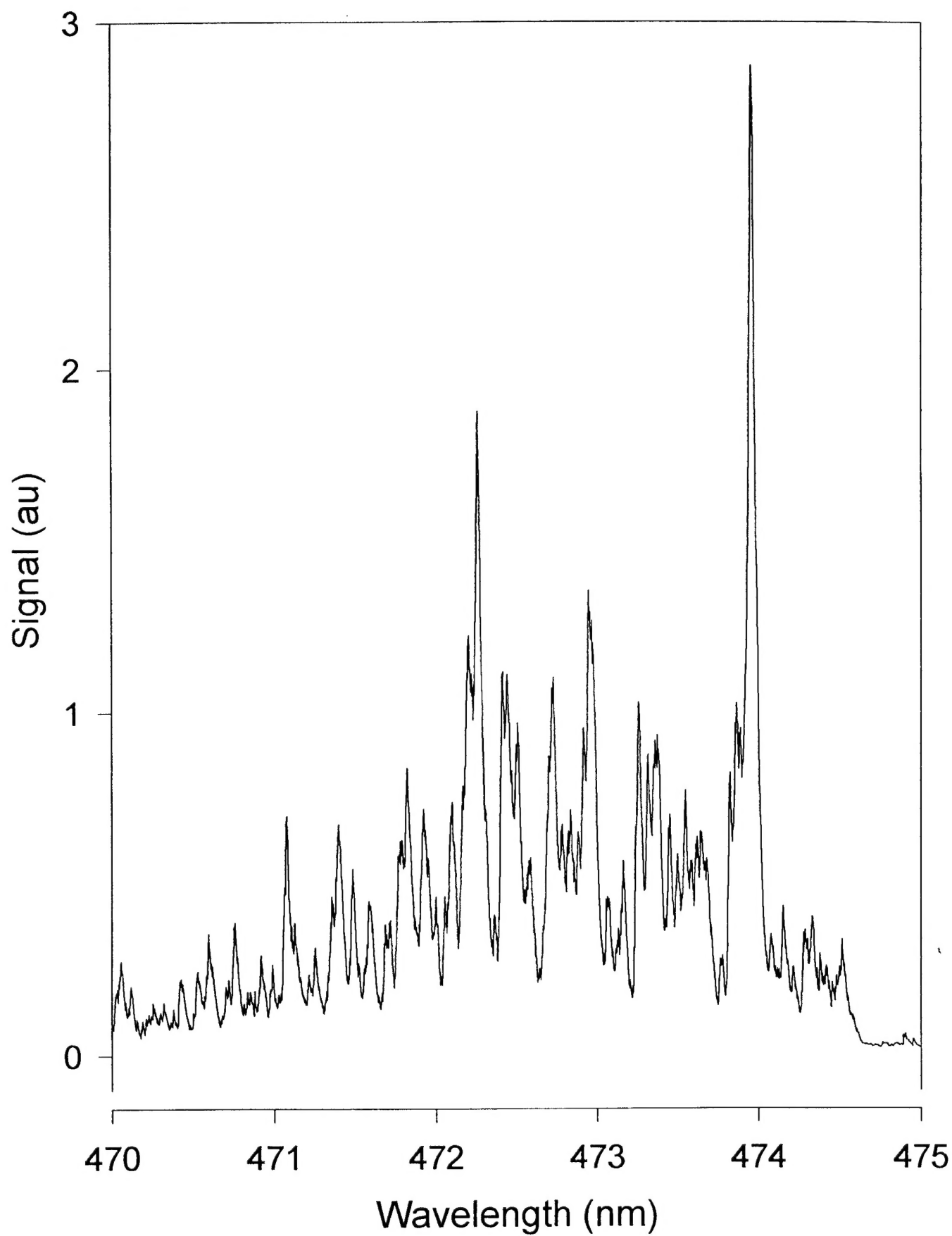
$\text{NO}_2$



# $\text{NO}_2$ ( NO A-X(0,1))



# NO A-X(0,1)



## A Critical Review of Laser Photofragmentation/Fragment Detection Techniques for Gas-Phase Chemical Analysis

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## ABSTRACT

A comprehensive review of Laser Photofragmentation/Fragment Detection techniques for spectrochemical analysis is presented. The techniques involve one and/or multiple lasers for both photolysis of the analyte and detection of the characteristic daughter photofragments. Fragment detection is accomplished by laser-induced fluorescence, photoionization, prompt emission, stimulated emission, and/or laser ionization recombination emission techniques. Recent applications of these techniques for chemical analysis include the detection of analytes by their characteristic atomic and molecular fragments. Various techniques are compared and contrasted, and future applications in analytical chemistry are discussed. A key to the main acronyms and abbreviations used in the text is provided in a glossary at the end of this review.

## I. INTRODUCTION

Laser spectrometric techniques are important in chemical analysis because they offer real-time monitoring capabilities with high analytical sensitivity and selectivity. In recent years, there has been an increase in the number of analytical applications of laser photofragmentation/fragment detection (PF/FD)